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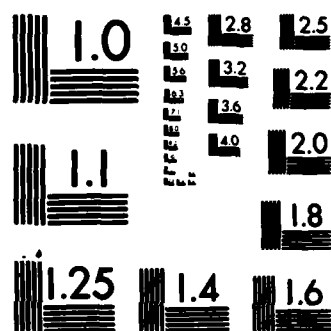
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Deactivation of Higher Vibrational Levels of HF by F Atoms

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23 April 1984

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This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

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CONTENTS

I.	INTRODUCTION.....	3
II.	EXPERIMENTAL APPARATUS AND PROCEDURE.....	5
III.	RESULTS.....	9
IV.	DISCUSSION.....	13
	REFERENCES.....	15

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FIGURES

1.	Schematic of the Apparatus.....	6
2.	Decay Rates of HF($v = 3$) vs. Decay Rates of HF($v = 1$).....	11

TABLE

1.	Relaxation Times Obtained for HF($v = 1$) and HF($v = 3$) with and without the Microwave Discharge.....	10
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I. INTRODUCTION

Since cw hydrogen fluoride (HF) lasers operate on the $F + H_2$ reaction, the excited $HF(v)$ molecules are produced in the presence of large concentrations of F atoms. Quigley and Wolga¹ have measured the rate coefficient for the deactivation of $HF(v = 1)$ by F atoms. However, the dependence on v of the $HF(v)$ - F deactivation rate has not been measured previously, and the theoretical models have not proved reliable for scaling to the higher vibrational levels. It has been found empirically²⁻⁵ that HF deactivation rate coefficients scale approximately as $v^{2.7}$ when the collision partner is a diatomic molecule and the deactivation process is an exothermic V-V or V-R,T process. The object of the present study is to determine the scaling with v of the $HF(v)$ - F deactivation rates.

In a study of $HF(v)$ deactivation by H atoms, Bott and Heidner⁶ found the rate coefficients for $HF(v)$ - H deactivation to scale approximately as 1:5:500 for $v = 1, 2$, and 3 , respectively. However, the interpretation of the rates of $HF(v = 3)$ removal by H atoms is complicated by the exothermic reaction



Also, the uncertainty in the ratio of $HF(v = 2)$ to $HF(v = 1)$ rate coefficients is rather large. Therefore, these data do not provide any degree of certainty to the $v^{2.7}$ scaling. Compared to HF self-deactivation, deactivation of $HF(v)$ by argon (Ar) and helium (He) is so slow⁷ at room temperature that no measurements have been made. The study of $HF(v)$ deactivation by F atoms has the advantage that the rate coefficients are much larger than those for Ar and He, without the complications of a reaction comparable to Reaction 1.

In the present study the laser-induced fluorescence technique has been used to determine the relative rates of F -atom deactivation of $HF(v = 3)$ and $HF(v = 1)$. A multiline pulsed HF laser was used to pump HF to $v = 1, 2$, and 3 by sequential photon absorption. The fluorescence decay times of these states in the presence of F atoms were used to determine the relative deactivation rates.

II. EXPERIMENTAL APPARATUS AND PROCEDURE

The technique of creating laser-induced fluorescence by means of sequential photon absorption has been used previously in this laboratory^{2,6} to study the deactivation of HF($v = 1, 2, 3$). In such experiments the multiline output of a pulsed HF laser passes through a fluorescence cell containing HF. A small fraction of the HF is pumped to $v = 1$ by the $1 \rightarrow 0$ laser transitions. Then, a fraction of this HF($v = 1$) is pumped to $v = 2$ and subsequently to $v = 3$ by $2 \rightarrow 1$ and $3 \rightarrow 2$ transitions, respectively. A schematic of the apparatus is shown in Fig. 1.

The HF($v = 1$) fluorescence was monitored with a Texas Instruments indium antimonide (InSb) detector. The signal across a 1-k Ω resistor was amplified by a factor of 15 with a Perry amplifier and recorded with a Biomation 805 transient recorder. The combined response time of the detector and its associated electronics was approximately 1.4 μ sec. The recorded signals were transferred to a Nicolet signal averager (model 1072), where 64 to 512 experimental signals were stored and averaged before being displayed on an x-y recorder. The detector was mounted transversely to the laser excitation beam, with the fluorescence focused onto the active element of the detector by means of 2-in.-diam f/1.5 calcium fluoride (CaF) optics.

The ($3 \rightarrow 0$) overtone emission from HF($v = 3$) was monitored with an RCA gallium arsenide (GaAs) photomultiplier mounted at the far end of the cell. The photomultiplier viewed the entire excited volume and collected 5 to 10 times more photons than when it was mounted in the transverse configuration of the infrared detector. It was protected from the direct HF laser pulse by a 0.63-cm-thick sheet of Plexiglas. A Kodak Wratten filter (87 C) cut out stray light while passing the $3 \rightarrow 0$ overtone emission. No fluorescence signal was measurable without HF flowing in the cell. A 47-k Ω load resistor and a Perry 070 amplifier (15 \times amplification) mounted directly on the end of the photomultiplier provided a response time of 2 μ sec. The photomultiplier signals were recorded with the Biomation 805 and averaged with the Nicolet 1072 signal averager.

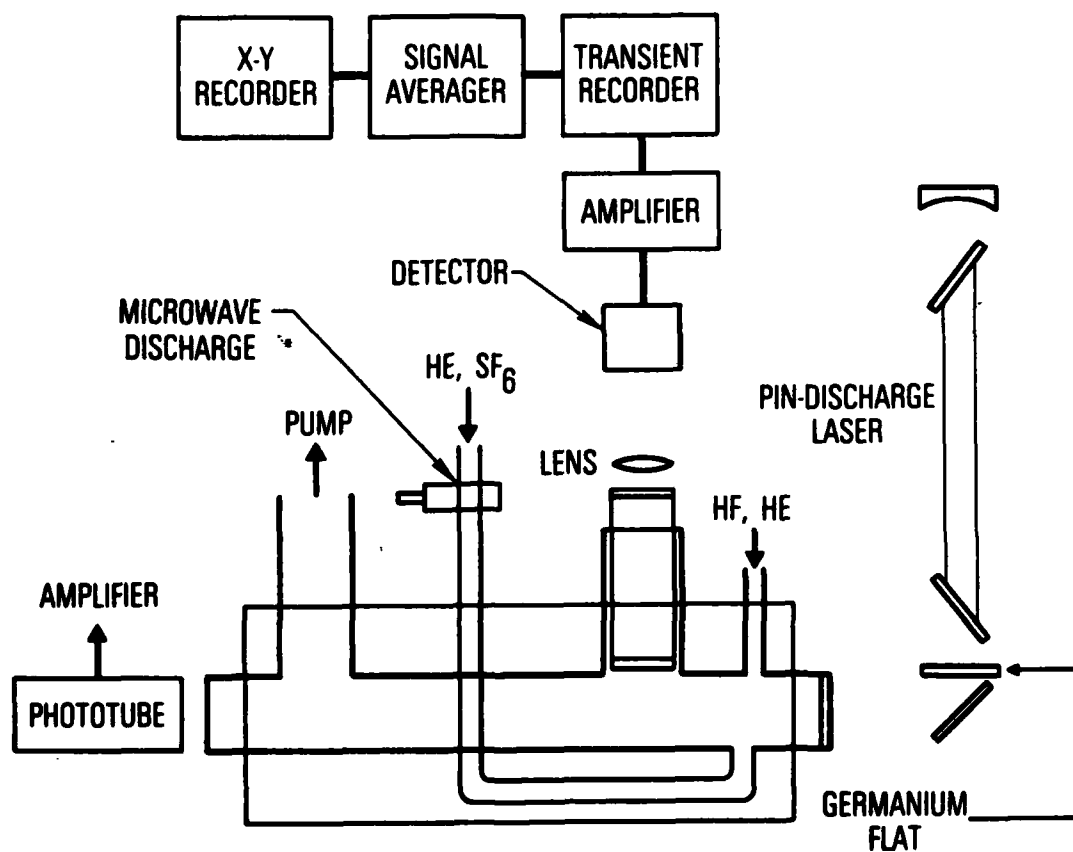


Fig. 1. Schematic of the Apparatus

The flow rates of the He and sulfur hexafluoride (SF_6) were measured with rotating-ball flow meters calibrated by pressure-rise measurements in a standard volume. Hydrogen fluoride was injected into the main flow through a small Teflon tube sealed into a stainless-steel coupling and regulated with a vernier needle valve. Most of the experiments were run with an SF_6 partial pressure of 0.16 Torr and a total pressure of 1.15 Torr. The latter was measured with a Baratron model 221 capacitance manometer. The HF partial pressure was estimated to be about 0.003 Torr.

The He (Air Products, 99.995%) was passed through a molecular sieve trap at LN_2 temperature; the trap was periodically baked out under vacuum at elevated temperature. The SF_6 (Matheson, 99.8%) was used without purification. The HF (Matheson, 99%, liquid phase) was purified by pumping on samples at 77 K to remove the noncondensibles and then was distilled into a Monel container.

Fluorine atoms were produced by a 2450-MHz microwave discharge (80 W) in a He- SF_6 gas mixture that flowed through a quartz discharge tube 10 mm in inner diameter (i.d.) and 20 cm in length. The discharge tube was connected to the main flow tube approximately 7 cm upstream of the region where the laser-induced fluorescence of $\text{HF}(v = 1)$ was monitored. The flow velocity in the 44-mm-i.d. fluorescence cell was approximately 300 cm/sec. The walls of the cell and the discharge tube (except for the discharge region itself) were coated with halocarbon wax in order to reduce the losses of F atoms and HF on the walls. The F atom concentration, as determined by the effect on the decay rate of $\text{HF}(v = 1)$, increased with microwave power and the SF_6 flow rate. It decreased somewhat when the flow was throttled to 5 Torr or when the He flow rate was increased by a factor of three.

For the $\text{HF}(v = 1)$ fluorescence measurements, the laser was operated without an output coupler and at a reduced H_2 flow rate. This increased the intensity of the $\text{HF}(v = 1)$ fluorescence and killed the direct laser pumping of $\text{HF}(v = 3)$. The $\text{HF}(v = 3)$ fluorescence due to V-V pumping was still observed, but the intensity was much reduced. For these conditions of lower $\text{HF}(v = 3)$ and presumably lower $\text{HF}(v = 2)$ concentrations, the fluorescence traces at

2.7 μm were less likely to exhibit the nonexponential decays associated with cascading from the upper vibrational levels. The higher-intensity traces also reduced the number of traces required for signal averaging. The HF($v = 3$) measurements were performed with a germanium (Ge) flat-output coupler, and with the H_2 flow rate adjusted to optimize the $v = 3$ fluorescence. For these conditions the HF($v = 3$) was pumped directly by the laser and decayed exponentially.

The procedure was to adjust the laser for $v = 1$ pumping and to record the $v = 1$ fluorescence with and without the microwave discharge. The optical cavity and gas flows in the laser were then changed for $v = 3$ pumping, and the $v = 3$ fluorescence was recorded with and without the microwave discharge. This cycle was then repeated.

III. RESULTS

Sulfur hexafluoride is an inefficient deactivator of HF($v = 1$), as it has a rate coefficient estimated⁸ to be $< 5 \times 10^{-5} (\mu\text{sec Torr})^{-1}$. The partial pressure of 0.16 Torr of SF₆ should contribute $< 0.8 \times 10^{-5} \mu\text{sec}^{-1}$ to the decay rates of $\sim 5 \times 10^{-4} \mu\text{sec}^{-1}$ observed without the microwave discharge. A small effect on the decay rates of $v = 1$ and $v = 3$ was observed when SF₆ was added to the flow. However, this effect was usually less than 10% and may have resulted from changes in the HF partial pressures. Kwok and Cohen⁹ reported a value of $1 \times 10^{-3} (\mu\text{sec Torr})^{-1}$ for the rate coefficient of HF($v = 3$) deactivation by SF₆. This would contribute $0.16 \times 10^{-3} \mu\text{sec}^{-1}$ to the decay rate of 3 to 4×10^{-3} observed for HF($v = 3$) without the microwave discharge.

Since SF₆ does not contribute greatly to the deactivation of HF(v), we can neglect the effect of removing part of it in the microwave discharge. The discharge breaks up a fraction of the SF₆, producing F atoms and most likely sulfur tetrafluoride (SF₄), the next stable SF compound. Since the heavy fluorinated compounds have been observed⁸ to be inefficient deactivators of HF, SF₄ can be expected to be inefficient also. Therefore, we will make the approximation

$$1/\tau_{\text{on}} - 1/\tau_{\text{off}} = \Delta\tau^{-1} = kP_F \quad (2)$$

where τ_{on} and τ_{off} are the decay times of the fluorescence with and without the discharge, k is the rate coefficient for HF(v) deactivation by F atoms, and P_F is the partial pressure of the F atoms. The ratio of the rate coefficients for HF($v = 3$) and HF($v = 1$) deactivation is calculated from the ratio of the $\Delta\tau^{-1}$ values obtained for HF($v = 3$) and HF($v = 1$). The exponential decay times for HF($v = 1$) and HF($v = 3$) with and without the microwave discharge are listed in Table 1. They were used to calculate the rate coefficient ratios, which had an average value of 20.8 with a standard deviation of 2.0. The decay rates of HF($v = 3$) are plotted against those of HF($v = 1$) in Fig. 2.

Table 1. Relaxation Times Obtained for HF($v = 1$) and HF($v = 3$) with and without the Microwave Discharge

τ_1 , μsec		τ_3 , μsec		$\Delta\tau_1^{-1} \times 10^4$, μsec^{-1}	$\Delta\tau_3^{-1} \times 10^3$, μsec^{-1}	$\Delta\tau_3^{-1}/\Delta\tau_1^{-1}$
On	Off	On	Off			
1018	1814	83	246	4.2	8.0	18.9
1240	2086	91	247	3.3	6.9	21.2
1179	2096	91	256	3.7	7.1	19.1
1222	2147	93	263	3.5	7.0	20.0
1222	2060	96	264	3.3	6.6	20.0
1260	2147	89	317	3.3	6.6	20.0
1391	2580	114	363	3.3	6.0	18.0
1552	2439	119	338	2.3	5.4	23.5
1441	2620	113	338	3.1	5.9	19.0
1169	2117	87	347	3.8	8.7	22.9
1220	2358	91	379	4.0	8.4	21.0
1089	2190	84	418	4.6	9.6	20.9

Average ratio of HF($v = 3$) to HF($v = 1$) decay rate = 20.8

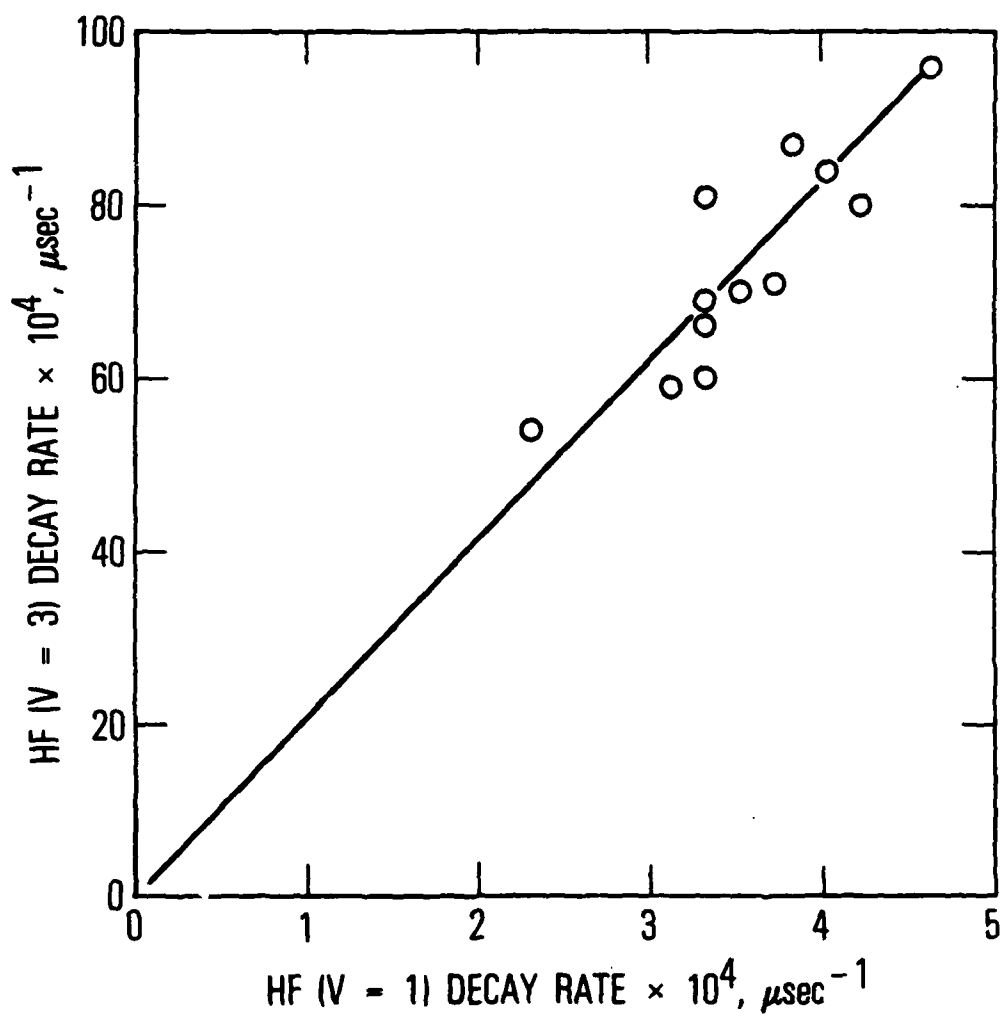


Fig. 2. Decay Rates of HF(v = 3) vs. Decay Rates of HF(v = 1)

The slope of the data is in agreement with the average of the individual ratios. The range of conditions was limited by the number of F atoms produced by the microwave discharge on one hand, and by the deactivation times observed with no discharge on the other hand. Somewhat longer relaxation times could be obtained at lower HF concentrations. (Nominal conditions were estimated to be about 0.003 Torr of HF.) However, lower signals obtained at lower HF concentrations required larger numbers of experiments for signal averaging.

Quigley and Wolga¹ obtained a rate coefficient of $1.7 \times 10^{11} \text{ cm}^3/\text{mol sec}$ [$1.0 \times 10^{-2} (\mu\text{sec Torr})^{-1}$] for the $\text{HF}(v = 1) - \text{F}$ deactivation rate coefficient. This value and values of 2.3×10^{-4} to $4.6 \times 10^{-4} \mu\text{sec}^{-1}$ for $\Delta\tau^{-1}$ obtained for $\text{HF}(v = 1)$ would indicate a partial pressure of 0.023 to 0.046 Torr of F atoms. A 7-to-15% breakup of SF_6 down to SF_4 would produce this concentration of F atoms.

IV. DISCUSSION

The rate coefficient for $\text{HF}(v = 3)$ deactivation by F atoms was found to be faster than that of $\text{HF}(v = 1)$ deactivation by a factor of 20.8 ± 2.0 . Within the uncertainties of the measurements the ratio of 20.8 is in good agreement with the ratios obtained previously for the diatomic molecules of nitrogen (N_2), oxygen (O_2), deuterium (D_2), and hydrogen chloride (HCl).^{2,10} If the rate coefficients scale as v^n , this ratio implies that $n = 2.76 \pm 0.09$. Other investigators^{3,4,5} have reported data for vibrational levels higher than $v = 3$ which also obey the $v^{2.7}$ scaling. Deactivation rates for $\text{DF}(v = 1 \text{ to } 4)$ have been found¹¹ to scale as v^n , where $n = 1.9$ to 2.0 for exothermic V-V or V-R,T deactivation processes. The scaling does not appear to be sensitive to temperature,^{2,3} at least at the reasonably low temperatures of 200 through 800 K.

The theoretical implications of the v^n scaling of the deactivation rate coefficients have been discussed in Ref. 11 and will not be repeated here in detail. On the basis of HCl and deuterium chloride (DCl) relaxation rates, Chen and Moore¹² proposed a deactivation mechanism in which the vibrational energy is converted to rotational energy of the initially excited molecule. For such a deactivation mechanism, the scaling with v could be expected to depend on the anharmonicity of the excited molecule and its rotational spacing, and not on the properties of the collision partner. Therefore, the scaling should be the same for atomic and diatomic collision partners (excluding endothermic V-V energy transfer processes). We now have deactivation rate data for an atomic collision partner as well as for a variety of diatomic collision partners. In spite of the variety of masses, vibrational frequencies, interaction potentials, etc., these rate coefficients scale as $v^{2.7}$ for $v = 1$ to 3.

Wilkins' trajectory calculations of $\text{HF}(v = 1)$ deactivation by F atoms¹³ resulted in a rate coefficient of $4.7 \times 10^{10} \text{ cm}^3/\text{mol sec}$ at 300 K, somewhat lower than the value of $1.7 \times 10^{11} \text{ cm}^3/\text{mol sec}$ obtained by Quigley and Wolga.¹ His rate coefficients increased roughly as v instead of as the $v^{2.7}$ observed in the present study. Later studies by Wilkins¹⁴ indicate such

calculations may be sensitive to details of the potential surface, which might account for the failure to predict the v dependence.

Although the $v^{2.7}$ scaling is faster than that recommended¹⁵ in the past, the extent of the effect on laser performance will require computer modeling calculations. Both HF and H are efficient deactivators of HF($v = 3$) and can be expected to dominate F-atom deactivation in regions where the HF and H concentrations have had a chance to build up.

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